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(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

CORRECTED VERSION

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
26 October 2000 (26.10.2000)

PCT

(10) International Publication Number
WO 00/63456 A3

(51) International Patent Classification[7]: C23C 2/00, H01L 39/00, H01B 12/00

(21) International Application Number: PCT/US00/10464

(22) International Filing Date: 18 April 2000 (18.04.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

60/130,079	20 April 1999 (20.04.1999)	US
60/144,430	16 July 1999 (16.07.1999)	US
60/165,099	12 November 1999 (12.11.1999)	US
09/532,362	21 March 2000 (21.03.2000)	US

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(81) Designated States *(national)*: CN, JP.

(84) Designated States *(regional)*: European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published:
— *with international search report*

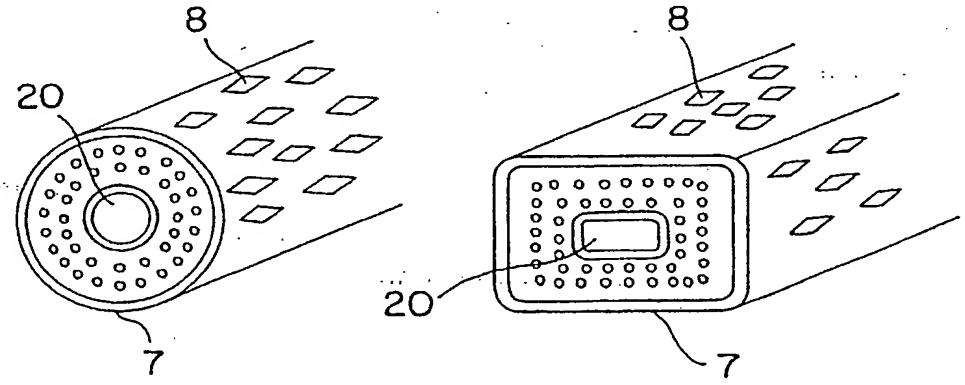
(88) Date of publication of the international search report:
2 August 2001

(48) Date of publication of this corrected version:
2 May 2002

(15) Information about Correction:
see PCT Gazette No. 18/2002 of 2 May 2002, Section II

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: CONSTRAINED FILAMENT NIOBIUM-BASED SUPERCONDUCTOR COMPOSITE AND PROCESS OF FABRICATION



(57) Abstract: A niobium-based superconductor is manufactured by establishing multiple niobium components in a billet of a ductile metal, working the composite billet through a series of reduction steps to form the niobium components into elongated elements, each niobium element having a thickness on the order of 1 to 25 microns, surrounding the billet prior to the last reduction step with a porous confining layer of an acid resistant metal, immersing the confined billet in an acid to remove the ductile metal from between the niobium elements while the niobium elements remain confined by said porous layer, exposing the confined mass of niobium elements to a material capable of reacting with Nb to form a superconductor.

WO 00/63456 A3

CONSTRAINED FILAMENT NIOBIUM-BASED SUPERCONDUCTOR COMPOSITE AND PROCESS OF FABRICATION

The present invention pertains to the fabrication of A-15 type multifilament composite superconductors (By "A-15" is meant the inter metallic compounds having βW structure).. These include Nb_3Sn, and Nb_3Al and are important because of their superior high field properties. Unfortunately, they are brittle compounds, difficult to make as fine filaments and as a result are very expensive. For these reasons, the ductile NbTi superconductors has dominated the commercial market even though its maximum magnetic field are limited to less than 8 Tesla. Significant improvements are needed in order to commercialize the A-15 conductors and to extend the useful magnetic fields to the 12 Tesla range on a cost effective basis. The present invention is also applicable to the production of the "B1" superconductors NbN and NbC.

A detailed description of present day methods currently being used in the industry is described in an article entitled "A-15 Superconductors" in the Metals Handbook, Tenth Edition, Volume 2 on pages 1060-1077, authored by David B. Smathers. Two processes are currently being used. One employs a bronze alloy as the matrix, the other a combination of pure copper and a pure Sn core. The first is known as the "Bronze Process" and the latter the "Internal Tin Process". The bronze matrix contains up to 13% Sn work hardens rapidly and requires frequent annealing steps. These anneals are avoided with the internal tin process. However, the cold drawing in the Internal Tin process can result in poor bonding, degraded filament quality and poor yields. After final drawing and twisting, both types of conductors are heated to approximately 700°C for 200 hours or more to form Nb_3Sn. Magnets are made exclusively by the Wind and React method.

The current densities that are obtained are substantially below what is theoretically possible based on experimental short sample data. Contributing

to this problem is the low reaction temp of up to 700°C, requiring hundreds of hours of reaction heat treatment. As the Sn is depleted, the Sn gradient is reduced which further limits the reaction. Unreacted Nb in the Nb filament can be left and Kirkendall type voids are formed in the residual matrix resulting in a lowering of the current density and mechanical properties of the conductor.

Significant improvements are needed to improve the high field performance and to reduce the cost of these important A-15 conductors.

In the fabrication of Nb_3Sn superconducting wire, a barrier, usually tantalum or a tantalum alloy is employed to prevent tin contamination of the stabilizing copper on the exterior of the wire during heat treatment. The process is described in the article by David B. Smathers. While the porous metal sheath described in the present invention is similar to the barrier used in Nb_3Sn conductor fabrication, application of the technology in this invention is entirely unique.

US Patent Nos. 5,034,857 and 5,869,196 by Wong, discloses a novel approach to the production of very fine valve metal filaments, preferable tantalum, for capacitor use. The benefits of fine filaments relative to fine powders are higher purity, lower cost, uniformity of cross section, and ease of dielectric infiltration, while still maintaining high surface area for anodization. The uniformity of cross section results in capacitors with high specific capacitance, lower ESR and ESL, and less sensitivity to forming voltage and sintering temperature as compared to fine powder compacts. Other patents involving valve metal filaments and fibers, their fabrication, or articles made therefrom include US Patent Nos. 3,277,564 (Webber), 3,379,000 (Webber), 3,394,213 (Roberts), 3,567,407 (Yoblin), 3,698,863 (Roberts) 3,742,369 (Douglass), 4,502,884 (Fife), 5,306,462 (Fife) and 5,245,514 (Fife).

The prior art relating to the fabrication of A-15 conductors can be obtained by reading both Smather's article and "Filamentary A-15 Superconductors" by Masaki Suenaga and Alan F. Clark, Plenum Press, N.Y.

Cryogenic Material Series (published 1980). In this book, the article by C.H. Rosner, B.A. Zeitlin, R.CX. Schwall, M.S. Walker and G.M. Ozeryansky entitled "Review of Superconducting Activities at IGC on A-15 Conductors" pages 67-79, specifically summarizes the earlier developments. Initially, powder metallurgy methods were employed followed soon by surface diffusion of liquid Sn of both Nb tapes and wires. Allen 3,218,693 patented a method where Sn coated Nb ribbons and wire were reacted to form Nb_3Sn at temperatures between 800°C to 1000°C. Similar products were also made by General Electric and later by IGC. The Nb wires in cable form, were Sn dipped, wound into a magnet and reacted; D.F. Martin et al Patent No. 3,429,032. A subsequent article, by Scanlan and Fietz, "MultiFilamentary Nb_3Sn for Superconducting Generator application", IEEE Trans. MAG-11 page 287, March '75, describes fabrication of a Nb_3Sn cable employing electroplated Sn as the Sn source.

A new approach is necessary to improve the processing of Nb_3Sn conductors. In the early 1960's, pure Nb tapes, wires and cable were dipped in molten Sn baths which was then reacted at high temperatures to form Nb_3Sn. Because Nb_3Sn is brittle, a ductile substrate of unreacted Nb was left to permit handling and subsequent winding into magnets. However, the need for stable, fine filaments and twisted conductors soon made this method obsolete.

Wong's patent '196 describes a process used to manufacture Ta capacitors where Ta multifilaments are made in a constraining sheath. This process describes the removal of the copper matrix after the final forming operation. The advantages of the external sheath is that final packaging of the filaments are unnecessary since the filaments are now constrained and supported by the outer sheath. Furthermore, the area inside the sheath is exactly determined as is the volume fraction of Ta.

A precursor wire, containing fine Nb filaments enclosed in a constraining sheath which can act as a supporting structure is produced.

Upon the removal of the copper matrix, and employing a liquid Sn dipping process, Sn or a CuSn alloy is used to infiltrate and surround the Nb filaments. The significant advantage here is that the need for subsequent wire drawing is completely eliminated as is the co-processing and low yield difficulties of present day Nb_3Sn conductors. The ability to easily increase the Sn concentration can result in substantial improvement in current density over present day conductors. The sheath, in the preferred embodiments, is made of Nb although Ta and stainless steel could also be used. The sheath is fabricated by methods as described in US Patent No. 5,869,196 by Wong. The billet is processed in the normal manner by extrusion and wire drawing to the final size. The copper matrix is then removed from this precursor wire and replaced with a Sn or CuSn alloy matrix. Final reaction heat treatments are then used to convert the Nb to Nb_3Sn.

Fig. 1 is a schematic depiction of the primary billet used in the present invention, Fig. 1a showing a transverse cross section, and Fig. 1b showing a cutaway view revealing the longitudinal disposition of the billet components.

Fig. 2 is a schematic depiction of the transverse cross section of the secondary billet used in the process of the present invention.

Fig. 3 is a schematic depiction of the product of the preferred embodiment of the present invention, Fig. 3a showing the product as a cylindrical body, and Fig. 3b showing the product after shaping into a rectangular body.

Fig. 4 is similar to Fig. 3 but shows the internal copper core to achieve stabilization.

Figs. 5-9 show additional systems for constraining the niobium filaments during and after the step of acid leaching of the copper.

Fig. 10 is a schematic depiction of the primary billet used in the preferred embodiment of the present invention.

This invention is directed to the fabrication of the fine metal filaments for use as the base for reaction with tin (for example) to produce A-15

superconductors in situ. A very small body of constrained filaments and a method for manufacture are disclosed. The invention will be of greatest value in the superconductor industry, which seeks to develop increasingly high magnetic field A-15 superconductors. The metal is selected from among the metallic elements, niobium and in particular, the A-15 compounds of Nb. In a preferred form, the product of the present invention, the metal filaments are of a diameter less than 50 microns. They are constrained within a cylindrical sheath, also made of metal, which has a wall thickness of 100 microns or less. The metal that forms the sheath is preferably the same as that of the filaments, but it is not necessarily so; tantalum can be used as well as stainless steel. Multifilament conductors suitable for use as superconductors are formed through the reduction of a metal billet consisting of multiple filaments of an appropriate refractory metal, preferably niobium, contained within, and spaced apart by, a ductile metal, preferably copper. The Nb filaments are elongated and substantially parallel within the billet as shown in Fig. 2. The array of Nb filaments 4 within the billet is surrounded by a confining layer of metal 7. This metal 7 is preferably, but not necessarily, the same as that which forms the filaments. The metal layer 7 preferably completely surrounds the Nb filament array 4 circumferentially and runs the full length of the filaments. The layer is separated from the filament array 4 by the same ductile metal 6 (e.g. Cu) that serves to separate the filaments 4 from each other. This same ductile metal 6 can also form the surface of the billet, preventing exposure of the confining metal layer during heating etc. The billet is reduced by conventional means, such as extrusion and wire drawing. The confining metal sheath 7 is then perforated (as shown in Figs. 3a and 3b at 8) such that the mineral acid can readily diffuse through the porous layer and remove the ductile copper separating the Nb filaments. It is important that these perforations 8 should be designed such that the sheath retains its ability to restrain and support the loose Nb filaments 4. More importantly, they should not substantially weaken the strength or ductility of the entire composite.

Preferably, the perforation 8 can be accomplished by mechanically rolling the wire in a rolling mill with the desired perforation pattern in a continuous matter. Other means can be also employed, such as selective chemical etching, laser drilling, etc. as would be apparent to one skilled in the art. The constraining metal must be one that is inert to the acid used to dissolve the copper.

Typical shapes would be a circular Fig. 3a or rectangular cross section Fig. 3b. An advantage for the rectangular shape is that the distance for the acid to penetrate for complete copper removal is reduced. Internal copper stabilization can be introduced as shown in Fig. 4. The Ta clad copper appears as a central core with a Ta diffusion barrier layer and it also reduces the leaching time. Thereafter, the copper-free confined bundle of Nb filaments is infiltrated with liquid Sn or CuSn alloy to thoroughly coat and embed each Nb filament in a solid Sn or CuSn alloy matrix. The Sn is then reacted with Nb to form Nb_3Sn in a separate step. Temperatures between 700°C to 1100°C are used, both performed in an inert atmosphere or vacuum chamber. The Nb-filaments may be reacted partially, completely or it can be completed at a later stage in the manufacture, e.g. after cabling or winding in a magnet.

In one preferred form of the invention, the Nb filaments, at the completion of the mechanical reduction step, will have a diameter on the order of one to twenty-five microns. In this preferred final form of the composite, the Nb filaments are separated by the Cu matrix and the Nb-Cu structure is surrounded by a 50 micron or less thick layer of Nb having an effective porosity of 50% or less. When this composite is immersed in an acid leaching bath of HNO_3 and H_2O at 100°C, the copper is removed in about 60 min, leaving a bundle of micron size Nb filaments confined by a porous Nb sheath. When this copper-free mass of Nb filaments is immersed in a Sn alloy bath between 700°C to 1100°C the surface tension of the molten Sn bath and the capillarity of the bundle of Nb filaments enclosed within the sheath draws

the tin into the bundle where it completely surrounds each Nb filament. The Sn is then reacted with the Nb to form the Nb_3Sn compound at a later stage of manufacturing.

As will be apparent to one skilled in the field of metallurgy, this porosity can be achieved, for example, by mechanically perforating the confining layer wherein the perforations 8 are uniformly spaced about 0.25 mm apart with a diamond shape size of 0.13 mm x 0.25 mm, as shown in Figs. 3a and 3b.

When the acid leaching of the copper from the Nb-Cu matrix results in unacceptably high amounts of surface contamination on the Nb filaments, these contaminates can be removed by the techniques described on page 9, lines 38-55, in my earlier patent 5,869,169. Such deoxidation treatments may improve the wetting of the Nb filaments by the liquid Sn alloy as well.

Prior to copper removal, multiple strands of wire can be cabled together and compacted if required. This would avoid any mechanical damage to the Nb filaments because, in this condition, the wire with the Cu matrix is in its most ductile state. The completed cable can then be leached and Sn infiltrated.

The conductor of Example I contains within the niobium sheath 34.9% copper by volume. High percentage of copper, i.e., greater spacing between Nb filaments, would permit a more rapid rate of copper removal by chemical etching but would also lower the current density of the conductor. To maximize the current density, the etched conductor can be mechanically compacted to increase the overall volume fraction of Nb before infiltration.

The infiltration step is performed in a continuous fashion similar to that used for Sn dipped Nb tapes. The resident time in the Sn bath should be as short as possible, only long enough to allow the wire to reach temperature and to completely infiltrate and embed the filaments. This also avoids any early brittle Nb_3Sn formation and the potential damage that can result from further processing such as cabling, etc.

Approximately 2 wt% Nb is soluble in liquid Sn at 1000°C. Extended time in liquid Sn baths at these temps can result in some Nb loss. Because of this, the time for the infiltration should be very short. In addition, this can largely be avoided by saturating the Sn prior to infiltration by addition of pure Nb metal to the bath. This can be done for example by slowly running ribbons or wires of pure Nb through the process first. At temperatures below 950°C, other non-superconducting compounds can form rapidly. For these reasons the dipping temperatures should be at least 1000°C and above. It is also important that the wire be cooled rapidly after infiltration to avoid the formation of large grain size brittle intermetallic compounds of Cu and Sn. Large copper additions to the Sn bath and its effects on Nb_3Sn layer growth has been reported by J.S. Caslaw, Cryogenic, Feb. '71, pp. 51-59. The presence of Cu "catalyze" the Nb_3Sn reaction and improves the surface of the Nb_3Sn. Addition of up to 32%wt Cu resulted in substantial increase in Jc.

The Hc2 and Tc values of Nb_3Sn are influenced by the Nb alloy composition. It is well known that selective additions of Ti and Ta can increase these values. It's important to not only increase Hc2 and Tc but also the Jc properties through proper flux pinning mechanisms. Smathers and Swenaga's articles give detailed explanation of "Flux pinning" and the methods currently employed. All of these methods can be applied in this invention. Besides pure Nb, alloys of Nb-1%Zr, Nb-1.5%Ti, and Nb-7.5%Ta can be used. The Ta and Ti can also be added to the Nb by means of a thin surface layer of expanded Ta or Ti mesh. This would also help to reduce the possibility of bridging between filaments. The Sn bath would include in addition to Cu, smaller amounts of Mg and Ti.

The most important parameter determining the performance of Nb_3Sn conductors is its current density. In the field of High Energy Physic, accelerator magnets capable of operating in excess of 12 Tesla at 4.2°K are needed. The dipole magnets for the Large Hardon Collider accelerator being constructed at CERN can only operate at less than 10 Tesla at 1.9°K using

NbTi. For Nb_3Sn, the highest Jc values are currently being made by the Internal Sn process and values as high as 2070 A/mm² at 12 Tesla and 4.2°K have been reported. The bronze process appears to be limited to below 1,000 A/mm² and are thus not a factor. Values as high as 3,000 A/mm² are needed for the next generation of accelerator magnets.

The area within the diffusion barrier contains only three components; Nb, Cu and Sn. Increasing Jc can only be obtained by increase in the volume fraction of Nb. This requires a proportional reduction in copper which increase the Sn to Cu ratio. Copper simply acts as a carrier for the Sn; it does not by itself participate directly toward increasing Jc. It does however perform a vital function; that is to allow the successful co-processing of both the bronze and Internal Sn Nb_3Sn conductors. Intensive efforts directed over the past two decades toward optimizing the Nb:Cu:Sn ratios has all but reached its limits due to the concomitant decrease in its fabricability as the Sn fraction is increased. In the present invention, no such limitation exist. The matrix alloy can be varied between pure Sn to pure Cu. Fabricability is not an issue since the conductor is made initially with a pure copper matrix.

While the preferred method of application of the constraining sheath has been described, it is recognized that alternatively, the sheath can be separately applied to a finished copper niobium multi-filaments wire by mechanical means. Several additional techniques may be employed as shown in Figs. 5 through 9.

In Fig. 5, the constraining layer is spirally wrapped around the Cu-Nb composite with adequate spacing between the spirals to allow access by the leaching acid.

In Fig. 6, the constraining layer is woven in a braid around the Cu-Nb composite with an open weave.

In Figs. 7 and 9, the Cu-Nb composites are carried in grooves of a carrier element resistant to the leach, but sufficiently confining to constrain the Cu free Nb filaments.

In Fig. 8, a Cu-Nb cable is twisted and flattened and then partially surrounded by a constraining layer.

In all cases, the principal requirements of the constraining layer are to allow for sufficient porosity for copper removal by acid, to be resistant to nitric acid attack, to constrain and support the loose Nb filaments after Cu removal and for subsequent infiltration with Sn. The constraining metal must be one which will not react with Sn or, if Nb is used will be sufficiently thick so that it will not be all coverted to Nb_3Sn.

Transition metal carbides and nitrides such as NbN and NbC occur with the B1 (NACL) crystal structure. Niobium nitride has been shown to have a transition temperature approaching 19°K. These important compounds are described in "Treatise on Material Science and Technology", Vol. 14, Metallurgy of Superconducting Materials, 1979 edited by Thomas Luhman and David Dew-Hughes, pages 429-432.

The present invention can be employed for forming NbN. Exactly the same steps
are utilized, that of porous outer sheath surrounding a copper matrix with Nb filaments from which the copper matrix is removed. Instead of the Sn infiltration step, a nitrogen containing atmosphere is introduced in which the niobium filaments are converted into niobium nitride (NbN) at elevated temperatures.

From a practical point of view, the gaseous phase reaction is a simpler and cleaner process than the handling of liquid Sn in the temperature range of 1000°C. The NbN filaments can be used as reacted or may require a metal infiltration for improved stability reasons as described by L.T. Summers, J.R. Miller, "The Influence of Liquid Metal Infiltration on Superconducting Characteristics of Niobium Nitride," Advanced in Cyrogenic Eng., Vol. 34, pp. 835-842, 1987.

EXAMPLE I

19 holes 2 are drilled into a 15.3 cm diameter bar 1 of copper 63.5 cm long 1 as shown in Fig. 1a. The holes are 2.57 cm in diameter and run the length of the bar in parallel fashion. The pattern of holes is as shown in Fig. 1a. The shortest distance between any two holes is 5.08 mm. A 1.27 cm insert is machined into each end of the copper bar. The insets are necessary in order that a copper nose and tail may be attached later. The copper bar containing the holes, a copper nose, and a copper tail are etched clean in a nitric acid solution, they are rinsed in water, rinsed a second time in methanol, and are then dried. 19 niobium bars, 2.54 cm in diameter and 61 cm long 2 are wiped clean with acetone and are inserted into the holes in the copper bar 3. The nose and tail are tungsten inert gas (TIG) welded into place, and the billet is evacuated at a temperature of 427°C to a pressure of 10^{-6} torr. The billet is then sealed as shown in Fig. 1b.

In preparation for extrusion, the billet is heated at a temperature of 816°C for a period of three hours. The billet is then extruded to a diameter of 2.54 cm. The extruded rod is cropped to ensure uniformity, and the cropped rod is cold drawn at an areal reduction rate of 20% per die pass to a final hexagonal diameter of 3.48 mm. That is, the final wire shape is hexagonal and the distance from flat to flat across the hexagon is 3.48 mm. At this size, the niobium filament diameter is 0.61 mm.

The wire is straightened and cut to 61 cm lengths. Pure copper rod is drawn to 3.48 mm diameter hexagonal wire and is straightened and cut to 61 cm lengths in the same manner as the wire containing the Nb filaments. Both types of filaments are cleaned in nitric acid in the same manner as was the primary billet. 1045 of the Nb-containing filaments 4 are stacked in symmetrical fashion.

A section of 0.64 mm thick Nb sheer 7, 45.7 cm wide and 610 cm long, is wiped clean with acetone and is inserted circumferentially into a clean copper can 8 having an internal diameter 14.5 cm, an external diameter 16.5 cm, and a length of 63.5 cm 7. The sheet 7 overlays by 0.3 cm so as to ensure a

continuous layer. The long dimension of the sheet runs along the can length. The stack of filaments is inserted into the niobium-lined can (see Fig. 2) and the copper nose and tail are electron beam welded into place under a vacuum of 10^{-4} torr. The billet is then hot isostatically pressed at a pressure of 104 Mpa and temperature of 650°C for four hours. The isostatically pressed billet is machined to a diameter of 15.3 cm, and the billet is prepared for extrusion by heating for three hours at 816°C. The billet is then extruded to a diameter of 2.54 cm.

The extruded rod is cropped to ensure uniformity. It is then drawn at an areal reduction rate of 20% per die pass to a diameter of 1.02 mm and twisted. At this wire diameter, the diameter of the Nb filaments is 4.06 microns, and the thickness of the niobium sheath is 42.6 microns. The total volume fraction of Nb filaments within the Nb sheath is 34.9%.

Thereafter, the Nb outer sheath 7 is perforated by means such as slotted rolls as mentioned previously and the product is leached in HNO_3/H_2O at 100°C for 60 min. to remove the copper separating the Nb filaments. The copper-free mass of Nb filaments is then preferably immersed in a tin bath at 1000°C to allow for maximum fluidity and surface tension of the Sn bath. An inert atmosphere of Argon is used to avoid oxidation. Dipping resident time in the Sn bath should be as short as possible (less than 10 sec) to minimize Nb_3Sn formation at this stage and maximize the ductility for further processing; i.e. cabling.

EXAMPLE II

In Example I, a continuous sheath, as shown in Fig. 2, was employed and at the final size the conductor was mechanically perforated as shown in Figs. 3a and 3b to allow for the removal of the copper matrix by acid leaching followed by liquid tin infiltration at high temperatures. It was also shown that the sheath can be applied separately after the conductor has been fabricated by means of taping Fig. 5, Braiding Fig. 6, or by mechanically confining the conductor into a support structure as shown in Figs. 7, 8 and 9.

A simpler and considerably less expensive method has been found which accomplishes the same objective. The sheath is constructed exactly as in Example I except now a narrow opening is left which is parallel to and runs the length of the filaments shown in Fig. 10.

The size of the opening can be adjusted to permit rapid copper removal of the matrix by acid leaching and still retain the sheath's ability to constrain and support the filaments. Following the final reduction, twisting and copper removal, a product which is an exact duplicate of the taping example of Fig. 5 is remarkably produced. Several variations are possible in the sheath design. For example, more than one opening can be used.

The twisting action causes the outer filaments to stretch more than the inner strands and when the copper matrix is removed, the outer filaments are under tension and act to compress and constrain the inner bundle of filaments. It has been observed that untwisted or lightly twisted, the outer filaments will tend to exfoliate at the sheath opening.

This conductor was leached in a HNO_3/H_2O 50/50 acid solution at 100°C to completely remove the copper matrix. The following Cu-Sn alloys were then used for infiltration experiments:

Cu wt%	Sn wt%
87	13
67	33
50	50
25	75
20	80
10	90
0	100

Successful infiltration at 1000°C was obtained for all alloys with the exception of the 13% Sn alloy. This alloy has a liquidus temperature of 1000°C

and would have required a temperature of at least 1200°C which was beyond the temperature capability of our small laboratory furnace.

The 33% Sn alloy sample was subsequently heat treated at 675°C for 24 and 48 hours. Metallographic examination of the cross section for the 48 hour sample reveals a substantial Nb_3Sn reacted layer, averaging 4-6 micron in thickness both in the filaments and in the surrounding sheath.

As shown in Fig. 4, a central copper core can be used. As a typical requirement, up to 40% copper is needed to insure stable conductor performance. To prevent Sn contamination of the copper core, a Ta protective barrier is employed in Fig. 4. It should be recognized that this structure by itself contributes a significant amount of support and that together with the external sheath of this invention would combine to protect the fragile Nb_3Sn filaments inside. It has been shown that a high strength copper containing Nb composite has been successfully used in conjunction with Nb_3Sn conductors and can be used in place of pure copper. (See advances in Cryogenic Eng., Vol. 42, Plenum Press, NY 1996, pages 1423-1432).

1. A process for manufacturing a Nb_3Sn superconductor comprising the steps of establishing multiple niobium components in a billet of a ductile metal, working the composite billet through a series of reduction steps to form said niobium components into elongated elements, each said element having a thickness on the order of 1 to 25 microns, surrounding said billet with a porous confining layer of an acid resistant metal, immersing said confined billet in an acid to remove said ductile metal from between the niobium elements while the niobium elements remain confined by said porous layer, immersing the confined mass of niobium elements in a liquid metal containing tin to coat said niobium elements with said liquid metal and subsequently reacting said tin with the Nb filaments to form NB_3Sn.

2. The process of claim 1 wherein said reaction is accomplished after said filaments are formed into a magnetic coil.

3. The process of claim 1 wherein the liquid metal bath is pure tin.

4. The process of claim 1 wherein the liquid metal bath is a copper alloy containing up to 95 wt% Sn.

5. The process of claim 1 wherein the liquid metal bath is a copper alloy containing up to 95 wt% Sn and at least 13 wt% Sn.

6. A process for manufacturing a niobium-based superconductor selected from the group consisting of Nb_3Sn, Nb_3Al, NbN, and NbC comprising the steps of establishing multiple niobium components in a billet of a ductile metal, working the composite billet through a series of reduction steps to form said niobium components into elongated elements, each said element having a thickness on the order of 1 to 25 microns, surrounding said billet with a porous confining layer of an acid resistant metal, immersing said confined billet in an acid to remove said ductile metal from between the niobium elements while the niobium elements remain confined by said porous layer, exposing the confined mass of niobium elements to a material capable of reacting with Nb to form a superconductor.

7. The process of claim 6 wherein said material is nitrogen.

8. A process for manufacturing a A-15 or B1 type compound superconductor comprising the steps of establishing multiple primary metal component in a billet of a ductile metal, working the composite billet through a series of reduction steps to form said primary metal components into elongated elements, each said element having a thickness in the order of 1 to 25 microns, surrounding said elements with a porous confining layer of an acid resistant metal, immersing said confined elements in an acid to remove said ductile metal from between the primary metal elements while the primary elements remain confined by said porous layer, contacting the confined mass of primary metal elements with a reactant and reacting the primary metal elements with the reactant to form the A-15 or B1 superconducting compound.

9. The process of claim 1 wherein said billet is surrounded by said porous layer prior to the last reduction step.

10. The process of claim 1 wherein said porous layer is created by twisting the reduced billet so that outer elements in the billet serve to confine inner elements in the billet when the ductile metal is removed from the billet.

11. The process of claim 1 wherein said porous layer is created by running at least one outer element along the outer surface of the reduced billet and twisting the reduced billet so that outer elements in the billet serve to confine inner elements in the billet when the ductile metal is removed from the billet.

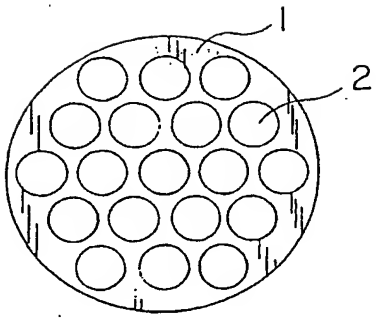


FIG. 1A

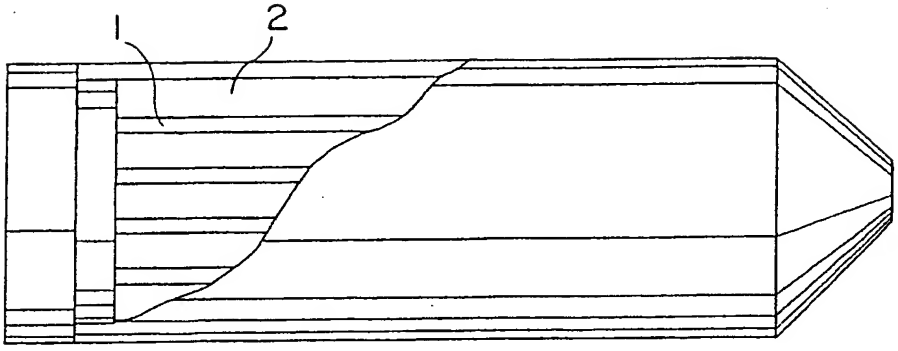


FIG. 1B

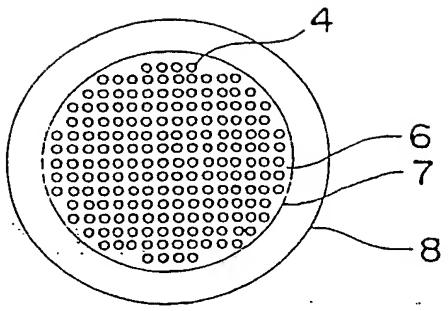


FIG. 2

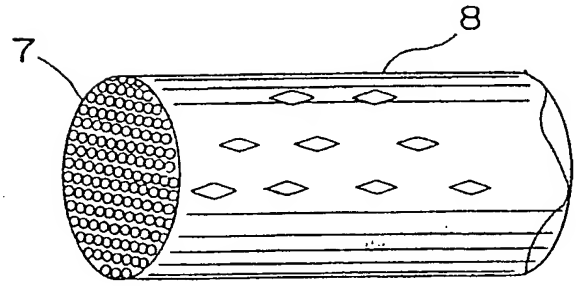


FIG. 3A

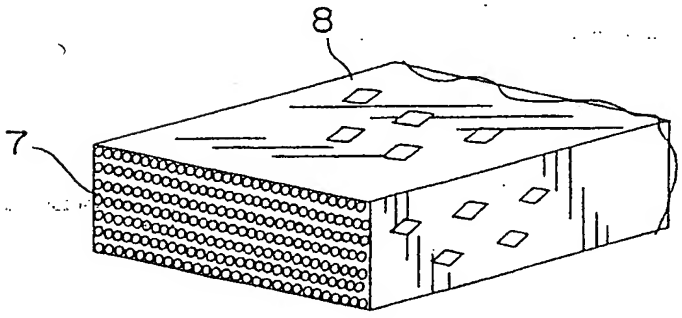


FIG. 3B

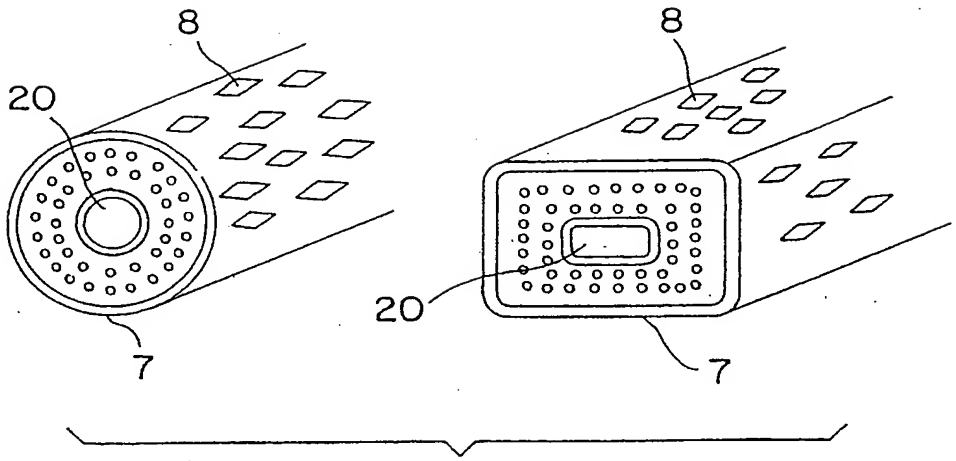


FIG. 4

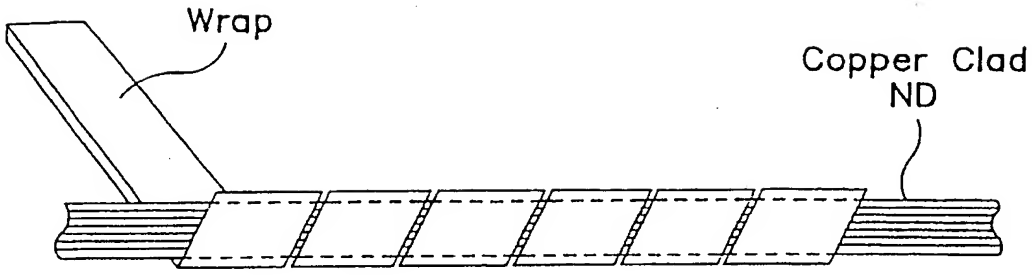


FIG. 5

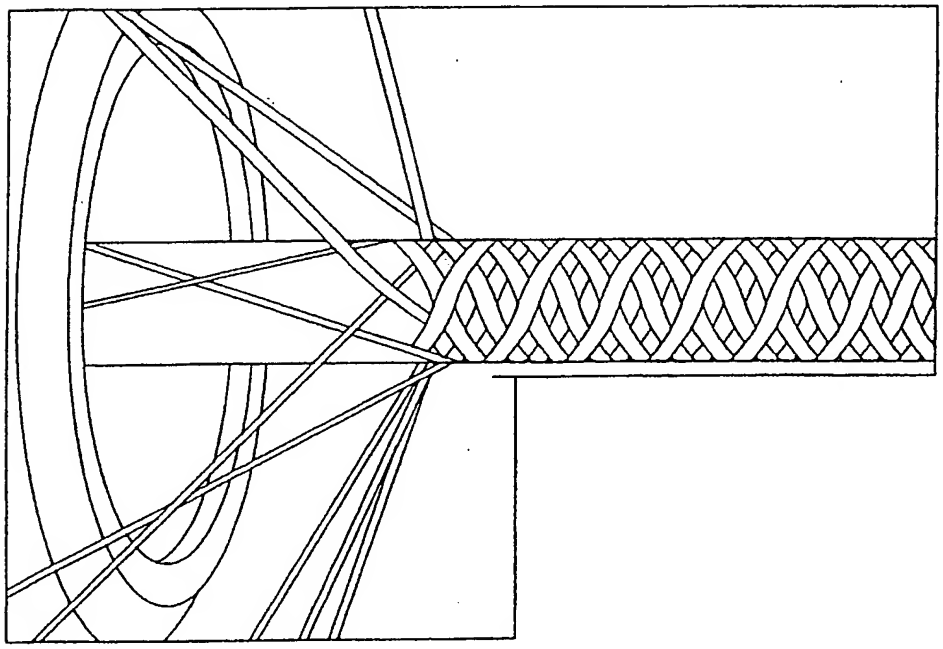


FIG. 6

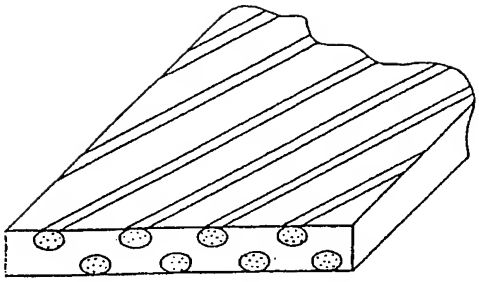


FIG. 7

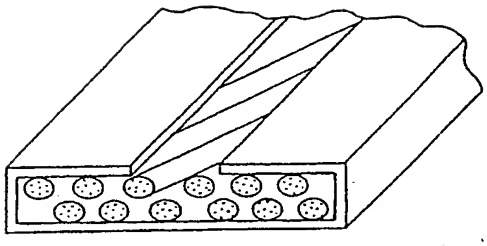


FIG. 8

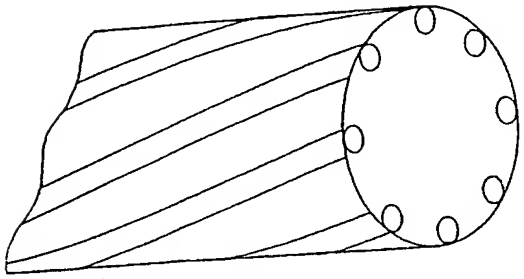


FIG. 9

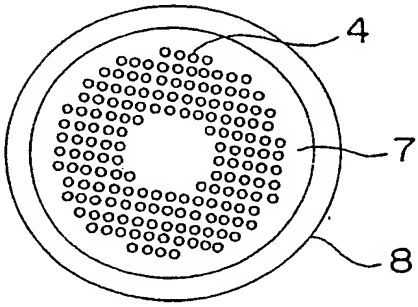


FIG. 10

INTERNATIONAL SEARCH REPORT

International Application No
PC./US 00/10464

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C23C2/00 H01L39/00 H01B12/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C23C B32B H01L H01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
WPI Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 534 219 A (MARANCIK WILLIAM G ET AL) 9 July 1996 (1996-07-09) the whole document ---	1-11
A	US 5 174 831 A (RUDZIAK MARK K ET AL) 29 December 1992 (1992-12-29) the whole document ---	1-11
A	US 5 869 196 A (RUDZIAK MARK K ET AL) 9 February 1999 (1999-02-09) cited in the application the whole document -----	1-11

[ ] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
1 September 2000	20.10.00

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	BECK

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WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : C23C 2/00

A2

(11) International Publication Number: WO 00/63456

(43) International Publication Date: 26 October 2000 (26.10.00)

(21) International Application Number: PCT/US00/10464

(22) International Filing Date: 18 April 2000 (18.04.00)

(30) Priority Data:

60/130,079	20 April 1999 (20.04.99)	US
60/144,430	16 July 1999 (16.07.99)	US
60/165,099	12 November 1999 (12.11.99)	US
09/532,362	21 March 2000 (21.03.00)	US

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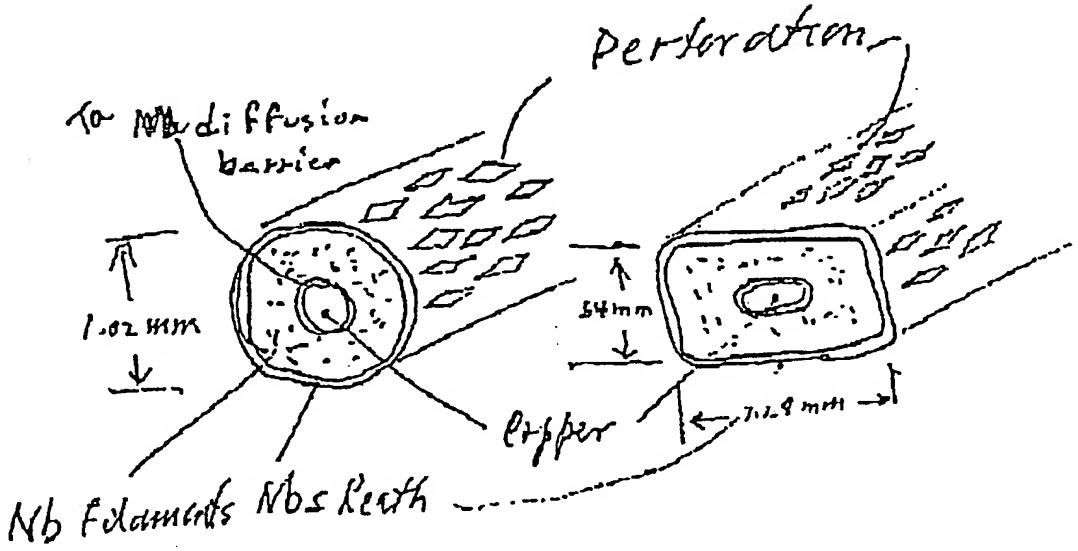
(81) Designated States: CN, JP, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published

Without international search report and to be republished upon receipt of that report.

(54) Title: CONSTRAINED FILAMENT NIOBIUM–BASED SUPERCONDUCTOR COMPOSITE AND PROCESS OF FABRICATION



(57) Abstract

A niobium–based superconductor is manufactured by establishing multiple niobium components in a billet of a ductile metal, working the composite billet through a series of reduction steps to form the niobium components into elongated elements, each niobium element having a thickness on the order of 1 to 25 microns, surrounding the billet prior to the last reduction step with a porous confining layer of an acid resistant metal, immersing the confined billet in an acid to remove the ductile metal from between the niobium elements while the niobium elements remain confined by said porous layer, exposing the confined mass of niobium elements to a material capable of reacting with Nb to form a superconductor.

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CONSTRAINED FILAMENT NIOBIUM-BASED SUPERCONDUCTOR COMPOSITE AND PROCESS OF FABRICATION

The present invention pertains to the fabrication of A-15 type multifilament composite superconductors (By "A-15" is meant the inter metallic compounds having βW structure). These include Nb_3Sn, and Nb_3Al and are important because of their superior high field properties. Unfortunately, they are brittle compounds, difficult to make as fine filaments and as a result are very expensive. For these reasons, the ductile NbTi superconductors has dominated the commercial market even though its maximum magnetic field are limited to less than 8 Tesla. Significant improvements are needed in order to commercialize the A-15 conductors and to extend the useful magnetic fields to the 12 Tesla range on a cost effective basis. The present invention is also applicable to the production of the "B1" superconductors NbN and NbC.

A detailed description of present day methods currently being used in the industry is described in an article entitled "A-15 Superconductors" in the Metals Handbook, Tenth Edition, Volume 2 on pages 1060-1077, authored by David B. Smathers. Two processes are currently being used. One employs a bronze alloy as the matrix, the other a combination of pure copper and a pure Sn core. The first is known as the "Bronze Process" and the latter the "Internal Tin Process". The bronze matrix contains up to 13% Sn work hardens rapidly and requires frequent annealing steps. These anneals are avoided with the internal tin process. However, the cold drawing in the Internal Tin process can result in poor bonding, degraded filament quality and poor yields. After final drawing and twisting, both types of conductors are heated to approximately 700°C for 200 hours or more to form Nb_3Sn. Magnets are made exclusively by the Wind and React method.

The current densities that are obtained are substantially below what is theoretically possible based on experimental short sample data. Contributing

to this problem is the low reaction temp of up to 700°C, requiring hundreds of hours of reaction heat treatment. As the Sn is depleted, the Sn gradient is reduced which further limits the reaction. Unreacted Nb in the Nb filament can be left and Kirkendall type voids are formed in the residual matrix resulting in a lowering of the current density and mechanical properties of the conductor.

Significant improvements are needed to improve the high field performance and to reduce the cost of these important A-15 conductors.

In the fabrication of Nb_3Sn superconducting wire, a barrier, usually tantalum or a tantalum alloy is employed to prevent tin contamination of the stabilizing copper on the exterior of the wire during heat treatment. The process is described in the article by David B. Smathers. While the porous metal sheath described in the present invention is similar to the barrier used in Nb_3Sn conductor fabrication, application of the technology in this invention is entirely unique.

US Patent Nos. 5,034,857 and 5,869,196 by Wong, discloses a novel approach to the production of very fine valve metal filaments, preferable tantalum, for capacitor use. The benefits of fine filaments relative to fine powders are higher purity, lower cost, uniformity of cross section, and ease of dielectric infiltration, while still maintaining high surface area for anodization. The uniformity of cross section results in capacitors with high specific capacitance, lower ESR and ESL, and less sensitivity to forming voltage and sintering temperature as compared to fine powder compacts. Other patents involving valve metal filaments and fibers, their fabrication, or articles made therefrom include US Patent Nos. 3,277,564 (Webber), 3,379,000 (Webber), 3,394,213 (Roberts), 3,567,407 (Yoblin), 3,698,863 (Roberts) 3,742,369 (Douglass), 4,502,884 (Fife), 5,306,462 (Fife) and 5,245,514 (Fife).

The prior art relating to the fabrication of A-15 conductors can be obtained by reading both Smather's article and "Filamentary A-15 Superconductors" by Masaki Suenaga and Alan F. Clark, Plenum Press, N.Y.

Cryogenic Material Series (published 1980). In this book, the article by C.H. Rosner, B.A. Zeitlin, R.CX. Schwall, M.S. Walker and G.M. Ozeryansky entitled "Review of Superconducting Activities at IGC on A-15 Conductors" pages 67-79, specifically summarizes the earlier developments. Initially, powder metallurgy methods were employed followed soon by surface diffusion of liquid Sn of both Nb tapes and wires. Allen 3,218,693 patented a method where Sn coated Nb ribbons and wire were reacted to form Nb_3Sn at temperatures between 800°C to 1000°C. Similar products were also made by General Electric and later by IGC. The Nb wires in cable form, were Sn dipped, wound into a magnet and reacted; D.F. Martin et al Patent No. 3,429,032. A subsequent article, by Scanlan and Fietz, "MultiFilamentary Nb_3Sn for Superconducting Generator application", IEEE Trans. MAG-11 page 287, March '75, describes fabrication of a Nb_3Sn cable employing electroplated Sn as the Sn source.

A new approach is necessary to improve the processing of Nb_3Sn conductors. In the early 1960's, pure Nb tapes, wires and cable were dipped in molten Sn baths which was then reacted at high temperatures to form Nb_3Sn. Because Nb_3Sn is brittle, a ductile substrate of unreacted Nb was left to permit handling and subsequent winding into magnets. However, the need for stable, fine filaments and twisted conductors soon made this method obsolete.

Wong's patent '196 describes a process used to manufacture Ta capacitors where Ta multifilaments are made in a constraining sheath. This process describes the removal of the copper matrix after the final forming operation. The advantages of the external sheath is that final packaging of the filaments are unnecessary since the filaments are now constrained and supported by the outer sheath. Furthermore, the area inside the sheath is exactly determined as is the volume fraction of Ta.

A precursor wire, containing fine Nb filaments enclosed in a constraining sheath which can act as a supporting structure is produced.

Upon the removal of the copper matrix, and employing a liquid Sn dipping process, Sn or a CuSn alloy is used to infiltrate and surround the Nb filaments. The significant advantage here is that the need for subsequent wire drawing is completely eliminated as is the co-processing and low yield difficulties of present day Nb_3Sn conductors. The ability to easily increase the Sn concentration can result in substantial improvement in current density over present day conductors. The sheath, in the preferred embodiments, is made of Nb although Ta and stainless steel could also be used. The sheath is fabricated by methods as described in US Patent No. 5,869,196 by Wong. The billet is processed in the normal manner by extrusion and wire drawing to the final size. The copper matrix is then removed from this precursor wire and replaced with a Sn or CuSn alloy matrix. Final reaction heat treatments are then used to convert the Nb to Nb_3Sn.

Fig. 1 is a schematic depiction of the primary billet used in the present invention, Fig. 1a showing a transverse cross section, and Fig. 1b showing a cutaway view revealing the longitudinal disposition of the billet components.

Fig. 2 is a schematic depiction of the transverse cross section of the secondary billet used in the process of the present invention.

Fig. 3 is a schematic depiction of the product of the preferred embodiment of the present invention, Fig. 3a showing the product as a cylindrical body, and Fig. 3b showing the product after shaping into a rectangular body.

Fig. 4 is similar to Fig. 3 but shows the internal copper core to achieve stabilization.

Figs. 5-9 show additional systems for constraining the niobium filaments during and after the step of acid leaching of the copper.

Fig. 10 is a schematic depiction of the primary billet used in the preferred embodiment of the present invention.

This invention is directed to the fabrication of the fine metal filaments for use as the base for reaction with tin (for example) to produce A-15

superconductors in situ. A very small body of constrained filaments and a method for manufacture are disclosed. The invention will be of greatest value in the superconductor industry, which seeks to develop increasingly high magnetic field A-15 superconductors. The metal is selected from among the metallic elements, niobium and in particular, the A-15 compounds of Nb. In a preferred form, the product of the present invention, the metal filaments are of a diameter less than 50 microns. They are constrained within a cylindrical sheath, also made of metal, which has a wall thickness of 100 microns or less. The metal that forms the sheath is preferably the same as that of the filaments, but it is not necessarily so; tantalum can be used as well as stainless steel. Multifilament conductors suitable for use as superconductors are formed through the reduction of a metal billet consisting of multiple filaments of an appropriate refractory metal, preferably niobium, contained within, and spaced apart by, a ductile metal, preferably copper. The Nb filaments are elongated and substantially parallel within the billet as shown in Fig. 2. The array of Nb filaments 4 within the billet is surrounded by a confining layer of metal 7. This metal 7 is preferably, but not necessarily, the same as that which forms the filaments. The metal layer 7 preferably completely surrounds the Nb filament array 4 circumferentially and runs the full length of the filaments. The layer is separated from the filament array 4 by the same ductile metal 6 (e.g. Cu) that serves to separate the filaments 4 from each other. This same ductile metal 6 can also form the surface of the billet, preventing exposure of the confining metal layer during heating etc. The billet is reduced by conventional means, such as extrusion and wire drawing. The confining metal sheath 7 is then perforated (as shown in Figs. 3a and 3b at 8) such that the mineral acid can readily diffuse through the porous layer and remove the ductile copper separating the Nb filaments. It is important that these perforations 8 should be designed such that the sheath retains its ability to restrain and support the loose Nb filaments 4. More importantly, they should not substantially weaken the strength or ductility of the entire composite.

Preferably, the perforation 8 can be accomplished by mechanically rolling the wire in a rolling mill with the desired perforation pattern in a continuous matter. Other means can be also employed, such as selective chemical etching, laser drilling, etc. as would be apparent to one skilled in the art. The constraining metal must be one that is inert to the acid used to dissolve the copper.

Typical shapes would be a circular Fig. 3a or rectangular cross section Fig. 3b. An advantage for the rectangular shape is that the distance for the acid to penetrate for complete copper removal is reduced. Internal copper stabilization can be introduced as shown in Fig. 4. The Ta clad copper appears as a central core with a Ta diffusion barrier layer and it also reduces the leaching time. Thereafter, the copper-free confined bundle of Nb filaments is infiltrated with liquid Sn or CuSn alloy to thoroughly coat and embed each Nb filament in a solid Sn or CuSn alloy matrix. The Sn is then reacted with Nb to form Nb_3Sn in a separate step. Temperatures between 700°C to 1100°C are used, both performed in an inert atmosphere or vacuum chamber. The Nb-filaments may be reacted partially, completely or it can be completed at a later stage in the manufacture, e.g. after cabling or winding in a magnet.

In one preferred form of the invention, the Nb filaments, at the completion of the mechanical reduction step, will have a diameter on the order of one to twenty-five microns. In this preferred final form of the composite, the Nb filaments are separated by the Cu matrix and the Nb-Cu structure is surrounded by a 50 micron or less thick layer of Nb having an effective porosity of 50% or less. When this composite is immersed in an acid leaching bath of HNO_3 and H_2O at 100°C, the copper is removed in about 60 min, leaving a bundle of micron size Nb filaments confined by a porous Nb sheath. When this copper-free mass of Nb filaments is immersed in a Sn alloy bath between 700°C to 1100°C the surface tension of the molten Sn bath and the capillarity of the bundle of Nb filaments enclosed within the sheath draws

the tin into the bundle where it completely surrounds each Nb filament. The Sn is then reacted with the Nb to form the Nb_3Sn compound at a later stage of manufacturing.

As will be apparent to one skilled in the field of metallurgy, this porosity can be achieved, for example, by mechanically perforating the confining layer wherein the perforations 8 are uniformly spaced about 0.25 mm apart with a diamond shape size of 0.13 mm x 0.25 mm, as shown in Figs. 3a and 3b.

When the acid leaching of the copper from the Nb-Cu matrix results in unacceptably high amounts of surface contamination on the Nb filaments, these contaminates can be removed by the techniques described on page 9, lines 38-55, in my earlier patent 5,869,169. Such deoxidation treatments may improve the wetting of the Nb filaments by the liquid Sn alloy as well.

Prior to copper removal, multiple strands of wire can be cabled together and compacted if required. This would avoid any mechanical damage to the Nb filaments because, in this condition, the wire with the Cu matrix is in its most ductile state. The completed cable can then be leached and Sn infiltrated.

The conductor of Example I contains within the niobium sheath 34.9% copper by volume. High percentage of copper, i.e., greater spacing between Nb filaments, would permit a more rapid rate of copper removal by chemical etching but would also lower the current density of the conductor. To maximize the current density, the etched conductor can be mechanically compacted to increase the overall volume fraction of Nb before infiltration.

The infiltration step is performed in a continuous fashion similar to that used for Sn dipped Nb tapes. The resident time in the Sn bath should be as short as possible, only long enough to allow the wire to reach temperature and to completely infiltrate and embed the filaments. This also avoids any early brittle Nb_3Sn formation and the potential damage that can result from further processing such as cabling, etc.

Approximately 2 wt% Nb is soluble in liquid Sn at 1000°C. Extended time in liquid Sn baths at these temps can result in some Nb loss. Because of this, the time for the infiltration should be very short. In addition, this can largely be avoided by saturating the Sn prior to infiltration by addition of pure Nb metal to the bath. This can be done for example by slowly running ribbons or wires of pure Nb through the process first. At temperatures below 950°C, other non-superconducting compounds can form rapidly. For these reasons the dipping temperatures should be at least 1000°C and above. It is also important that the wire be cooled rapidly after infiltration to avoid the formation of large grain size brittle intermetallic compounds of Cu and Sn. Large copper additions to the Sn bath and its effects on Nb_3Sn layer growth has been reported by J.S. Caslaw, Cryogenic, Feb. '71, pp. 51-59. The presence of Cu "catalyze" the Nb_3Sn reaction and improves the surface of the Nb_3Sn. Addition of up to 32%wt Cu resulted in substantial increase in Jc.

The Hc2 and Tc values of Nb_3Sn are influenced by the Nb alloy composition. It is well known that selective additions of Ti and Ta can increase these values. It's important to not only increase Hc2 and Tc but also the Jc properties through proper flux pinning mechanisms. Smathers and Swenaga's articles give detailed explanation of "Flux pinning" and the methods currently employed. All of these methods can be applied in this invention. Besides pure Nb, alloys of Nb-1%Zr, Nb-1.5%Ti, and Nb-7.5%Ta can be used. The Ta and Ti can also be added to the Nb by means of a thin surface layer of expanded Ta or Ti mesh. This would also help to reduce the possibility of bridging between filaments. The Sn bath would include in addition to Cu, smaller amounts of Mg and Ti.

The most important parameter determining the performance of Nb_3Sn conductors is its current density. In the field of High Energy Physic, accelerator magnets capable of operating in excess of 12 Tesla at 4.2°K are needed. The dipole magnets for the Large Hardon Collider accelerator being constructed at CERN can only operate at less than 10 Tesla at 1.9°K using

NbTi. For Nb_3Sn, the highest Jc values are currently being made by the Internal Sn process and values as high as 2070 A/mm² at 12 Tesla and 4.2°K have been reported. The bronze process appears to be limited to below 1,000 A/mm² and are thus not a factor. Values as high as 3,000 A/mm² are needed for the next generation of accelerator magnets.

The area within the diffusion barrier contains only three components; Nb, Cu and Sn. Increasing Jc can only be obtained by increase in the volume fraction of Nb. This requires a proportional reduction in copper which increase the Sn to Cu ratio. Copper simply acts as a carrier for the Sn; it does not by itself participate directly toward increasing Jc. It does however perform a vital function; that is to allow the successful co-processing of both the bronze and Internal Sn Nb_3Sn conductors. Intensive efforts directed over the past two decades toward optimizing the Nb:Cu:Sn ratios has all but reached its limits due to the concomitant decrease in its fabricability as the Sn fraction is increased. In the present invention, no such limitation exist. The matrix alloy can be varied between pure Sn to pure Cu. Fabricability is not an issue since the conductor is made initially with a pure copper matrix.

While the preferred method of application of the constraining sheath has been described, it is recognized that alternatively, the sheath can be separately applied to a finished copper niobium multi-filaments wire by mechanical means. Several additional techniques may be employed as shown in Figs. 5 through 9.

In Fig. 5, the constraining layer is spirally wrapped around the Cu-Nb composite with adequate spacing between the spirals to allow access by the leaching acid.

In Fig. 6, the constraining layer is woven in a braid around the Cu-Nb composite with an open weave.

In Figs. 7 and 9, the Cu-Nb composites are carried in grooves of a carrier element resistant to the leach, but sufficiently confining to constrain the Cu free Nb filaments.

In Fig. 8, a Cu-Nb cable is twisted and flattened and then partially surrounded by a constraining layer.

In all cases, the principal requirements of the constraining layer are to allow for sufficient porosity for copper removal by acid, to be resistant to nitric acid attack, to constrain and support the loose Nb filaments after Cu removal and for subsequent infiltration with Sn. The constraining metal must be one which will not react with Sn or, if Nb is used will be sufficiently thick so that it will not be all coverted to Nb_3Sn.

Transition metal carbides and nitrides such as NbN and NbC occur with the B1 (NACL) crystal structure. Niobium nitride has been shown to have a transition temperature approaching 19°K. These important compounds are described in "Treatise on Material Science and Technology", Vol. 14, Metallurgy of Superconducting Materials, 1979 edited by Thomas Luhman and David Dew-Hughes, pages 429-432.

The present invention can be employed for forming NbN. Exactly the same steps
are utilized, that of porous outer sheath surrounding a copper matrix with Nb filaments from which the copper matrix is removed. Instead of the Sn infiltration step, a nitrogen containing atmosphere is introduced in which the niobium filaments are converted into niobium nitride (NbN) at elevated temperatures.

From a practical point of view, the gaseous phase reaction is a simpler and cleaner process than the handling of liquid Sn in the temperature range of 1000°C. The NbN filaments can be used as reacted or may require a metal infiltration for improved stability reasons as described by L.T. Summers, J.R. Miller, "The Influence of Liquid Metal Infiltration on Superconducting Characteristics of Niobium Nitride," Advanced in Cyrogenic Eng., Vol. 34, pp. 835-842, 1987.

EXAMPLE I

19 holes 2 are drilled into a 15.3 cm diameter bar 1 of copper 63.5 cm long 1 as shown in Fig. 1a. The holes are 2.57 cm in diameter and run the length of the bar in parallel fashion. The pattern of holes is as shown in Fig. 1a. The shortest distance between any two holes is 5.08 mm. A 1.27 cm insert is machined into each end of the copper bar. The insets are necessary in order that a copper nose and tail may be attached later. The copper bar containing the holes, a copper nose, and a copper tail are etched clean in a nitric acid solution, they are rinsed in water, rinsed a second time in methanol, and are then dried. 19 niobium bars, 2.54 cm in diameter and 61 cm long 2 are wiped clean with acetone and are inserted into the holes in the copper bar 3. The nose and tail are tungsten inert gas (TIG) welded into place, and the billet is evacuated at a temperature of 427°C to a pressure of 10^{-6} torr. The billet is then sealed as shown in Fig. 1b.

In preparation for extrusion, the billet is heated at a temperature of 816°C for a period of three hours. The billet is then extruded to a diameter of 2.54 cm. The extruded rod is cropped to ensure uniformity, and the cropped rod is cold drawn at an areal reduction rate of 20% per die pass to a final hexagonal diameter of 3.48 mm. That is, the final wire shape is hexagonal and the distance from flat to flat across the hexagon is 3.48 mm. At this size, the niobium filament diameter is 0.61 mm.

The wire is straightened and cut to 61 cm lengths. Pure copper rod is drawn to 3.48 mm diameter hexagonal wire and is straightened and cut to 61 cm lengths in the same manner as the wire containing the Nb filaments. Both types of filaments are cleaned in nitric acid in the same manner as was the primary billet. 1045 of the Nb-containing filaments 4 are stacked in symmetrical fashion.

A section of 0.64 mm thick Nb sheer 7, 45.7 cm wide and 610 cm long, is wiped clean with acetone and is inserted circumferentially into a clean copper can 8 having an internal diameter 14.5 cm, an external diameter 16.5 cm, and a length of 63.5 cm 7. The sheet 7 overlays by 0.3 cm so as to ensure a

continuous layer. The long dimension of the sheet runs along the can length. The stack of filaments is inserted into the niobium-lined can (see Fig. 2) and the copper nose and tail are electron beam welded into place under a vacuum of 10^{-4} torr. The billet is then hot isostatically pressed at a pressure of 104 Mpa and temperature of 650°C for four hours. The isostatically pressed billet is machined to a diameter of 15.3 cm, and the billet is prepared for extrusion by heating for three hours at 816°C. The billet is then extruded to a diameter of 2.54 cm.

The extruded rod is cropped to ensure uniformity. It is then drawn at an areal reduction rate of 20% per die pass to a diameter of 1.02 mm and twisted. At this wire diameter, the diameter of the Nb filaments is 4.06 microns, and the thickness of the niobium sheath is 42.6 microns. The total volume fraction of Nb filaments within the Nb sheath is 34.9%.

Thereafter, the Nb outer sheath 7 is perforated by means such as slotted rolls as mentioned previously and the product is leached in HNO_3/H_2O at 100°C for 60 min. to remove the copper separating the Nb filaments. The copper-free mass of Nb filaments is then preferably immersed in a tin bath at 1000°C to allow for maximum fluidity and surface tension of the S_n bath. An inert atmosphere of Argon is used to avoid oxidation. Dipping resident time in the Sn bath should be as short as possible (less than 10 sec) to minimize Nb_3Sn formation at this stage and maximize the ductility for further processing; i.e. cabling.

EXAMPLE II

In Example I, a continuous sheath, as shown in Fig. 2, was employed and at the final size the conductor was mechanically perforated as shown in Figs. 3a and 3b to allow for the removal of the copper matrix by acid leaching followed by liquid tin infiltration at high temperatures. It was also shown that the sheath can be applied separately after the conductor has been fabricated by means of taping Fig. 5, Braiding Fig. 6, or by mechanically confining the conductor into a support structure as shown in Figs. 7, 8 and 9.

A simpler and considerably less expensive method has been found which accomplishes the same objective. The sheath is constructed exactly as in Example I except now a narrow opening is left which is parallel to and runs the length of the filaments shown in Fig. 10.

The size of the opening can be adjusted to permit rapid copper removal of the matrix by acid leaching and still retain the sheath's ability to constrain and support the filaments. Following the final reduction, twisting and copper removal, a product which is an exact duplicate of the taping example of Fig. 5 is remarkably produced. Several variations are possible in the sheath design. For example, more than one opening can be used.

The twisting action causes the outer filaments to stretch more than the inner strands and when the copper matrix is removed, the outer filaments are under tension and act to compress and constrain the inner bundle of filaments. It has been observed that untwisted or lightly twisted, the outer filaments will tend to exfoliate at the sheath opening.

This conductor was leached in a HNO_3/H_2O 50/50 acid solution at 100°C to completely remove the copper matrix. The following Cu-Sn alloys were then used for infiltration experiments:

Cu wt%	Sn wt%
87	13
67	33
50	50
25	75
20	80
10	90
0	100

Successful infiltration at 1000°C was obtained for all alloys with the exception of the 13% Sn alloy. This alloy has a liquidus temperature of 1000°C

and would have required a temperature of at least 1200°C which was beyond the temperature capability of our small laboratory furnace.

The 33% Sn alloy sample was subsequently heat treated at 675°C for 24 and 48 hours. Metallographic examination of the cross section for the 48 hour sample reveals a substantial Nb_3Sn reacted layer, averaging 4-6 micron in thickness both in the filaments and in the surrounding sheath.

As shown in Fig. 4, a central copper core can be used. As a typical requirement, up to 40% copper is needed to insure stable conductor performance. To prevent Sn contamination of the copper core, a Ta protective barrier is employed in Fig. 4. It should be recognized that this structure by itself contributes a significant amount of support and that together with the external sheath of this invention would combine to protect the fragile Nb_3Sn filaments inside. It has been shown that a high strength copper containing Nb composite has been successfully used in conjunction with Nb_3Sn conductors and can be used in place of pure copper. (See advances in Cryogenic Eng., Vol. 42, Plenum Press, NY 1996, pages 1423-1432).

1. A process for manufacturing a Nb_3Sn superconductor comprising the steps of establishing multiple niobium components in a billet of a ductile metal, working the composite billet through a series of reduction steps to form said niobium components into elongated elements, each said element having a thickness on the order of 1 to 25 microns, surrounding said billet with a porous confining layer of an acid resistant metal, immersing said confined billet in an acid to remove said ductile metal from between the niobium elements while the niobium elements remain confined by said porous layer, immersing the confined mass of niobium elements in a liquid metal containing tin to coat said niobium elements with said liquid metal and subsequently reacting said tin with the Nb filaments to form NB_3Sn.

2. The process of claim 1 wherein said reaction is accomplished after said filaments are formed into a magnetic coil.

3. The process of claim 1 wherein the liquid metal bath is pure tin.

4. The process of claim 1 wherein the liquid metal bath is a copper alloy containing up to 95 wt% Sn.

5. The process of claim 1 wherein the liquid metal bath is a copper alloy containing up to 95 wt% Sn and at least 13 wt% Sn.

6. A process for manufacturing a niobium-based superconductor selected from the group consisting of Nb_3Sn, Nb_3Al, NbN, and NbC comprising the steps of establishing multiple niobium components in a billet of a ductile metal, working the composite billet through a series of reduction steps to form said niobium components into elongated elements, each said element having a thickness on the order of 1 to 25 microns, surrounding said billet with a porous confining layer of an acid resistant metal, immersing said confined billet in an acid to remove said ductile metal from between the niobium elements while the niobium elements remain confined by said porous layer, exposing the confined mass of niobium elements to a material capable of reacting with Nb to form a superconductor.

7. The process of claim 6 wherein said material is nitrogen.

8. A process for manufacturing a A-15 or B1 type compound superconductor comprising the steps of establishing multiple primary metal component in a billet of a ductile metal, working the composite billet through a series of reduction steps to form said primary metal components into elongated elements, each said element having a thickness in the order of 1 to 25 microns, surrounding said elements with a porous confining layer of an acid resistant metal, immersing said confined elements in an acid to remove said ductile metal from between the primary metal elements while the primary elements remain confined by said porous layer, contacting the confined mass of primary metal elements with a reactant and reacting the primary metal elements with the reactant to form the A-15 or B1 superconducting compound.

9. The process of claim 1 wherein said billet is surrounded by said porous layer prior to the last reduction step.

10. The process of claim 1 wherein said porous layer is created by twisting the reduced billet so that outer elements in the billet serve to confine inner elements in the billet when the ductile metal is removed from the billet.

11. The process of claim 1 wherein said porous layer is created by running at least one outer element along the outer surface of the reduced billet and twisting the reduced billet so that outer elements in the billet serve to confine inner elements in the billet when the ductile metal is removed from the billet.

A niobium-based superconductor is manufactured by establishing multiple niobium components in a billet of a ductile metal, working the composite billet through a series of reduction steps to form the niobium components into elongated elements, each niobium element having a thickness on the order of 1 to 25 microns, surrounding the billet prior to the last reduction step with a porous confining layer of an acid resistant metal, immersing the confined billet in an acid to remove the ductile metal from between the niobium elements while the niobium elements remain confined by said porous layer, exposing the confined mass of niobium elements to a material capable of reacting with Nb to form a superconductor.

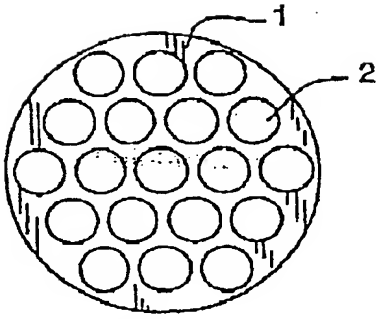

FIG. 1a

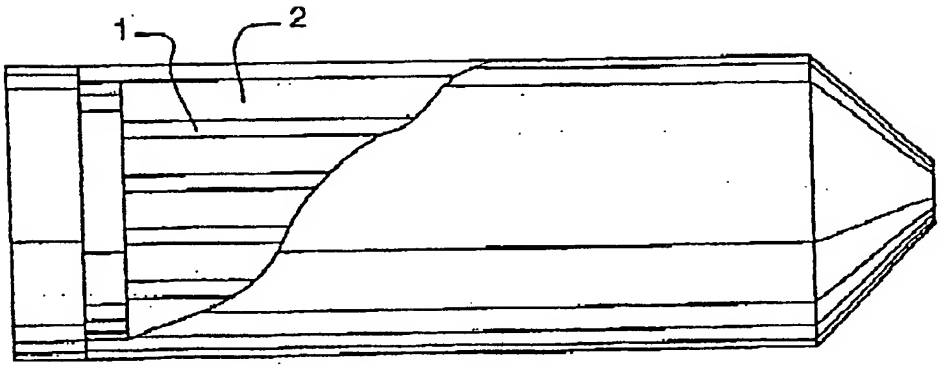

FIG. 1b

FIG. 1

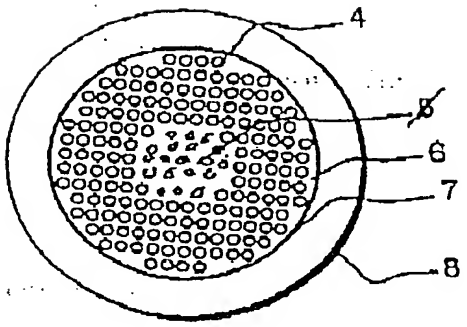

FIG. 2

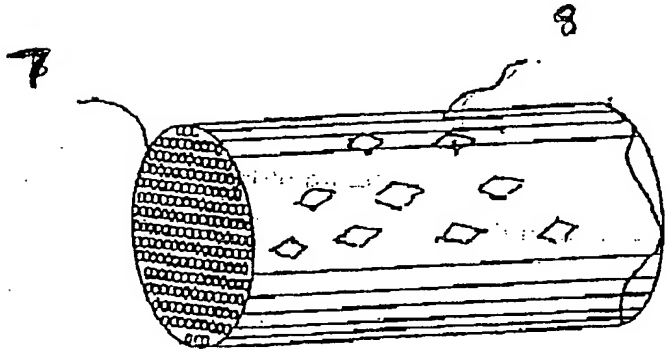

FIG. 3a

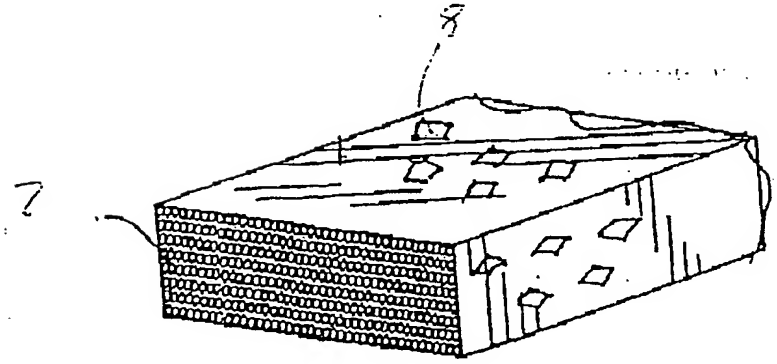

FIG. 3b

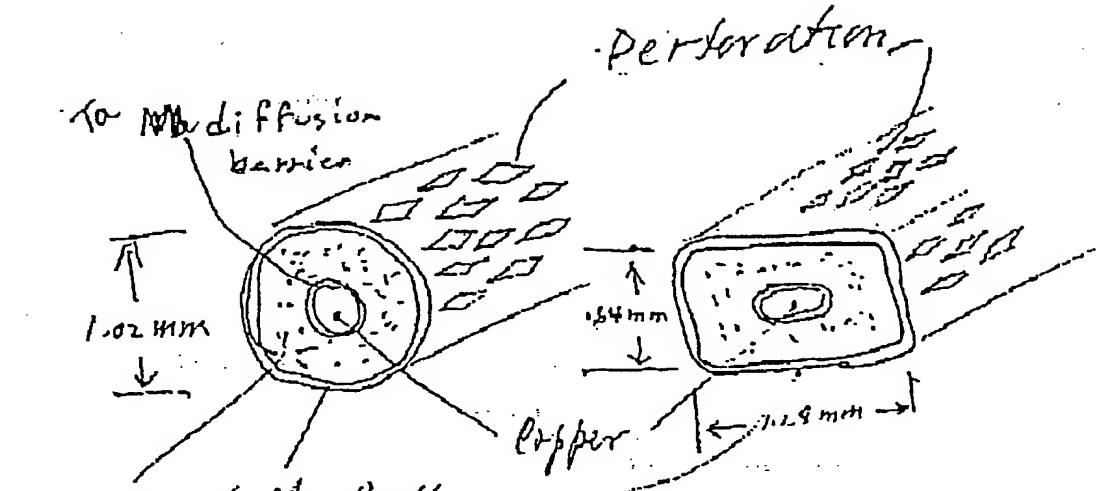
Perforation
To Nb diffusion barrier
1.02 mm
0.64 mm
Copper
Nb Filaments Nb-Zr with

Fig 4

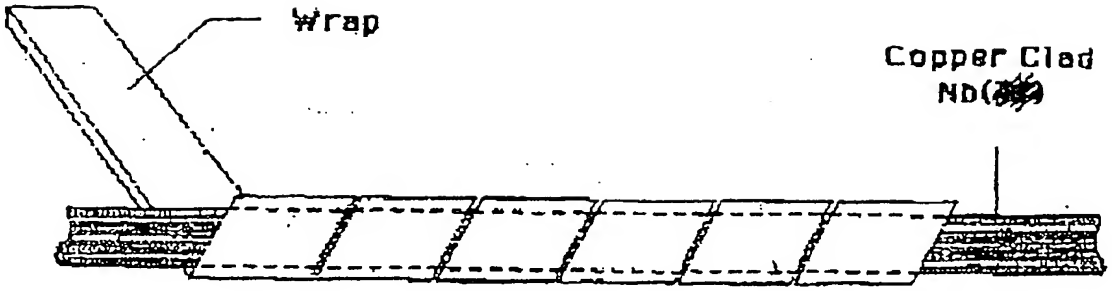

Fig 5

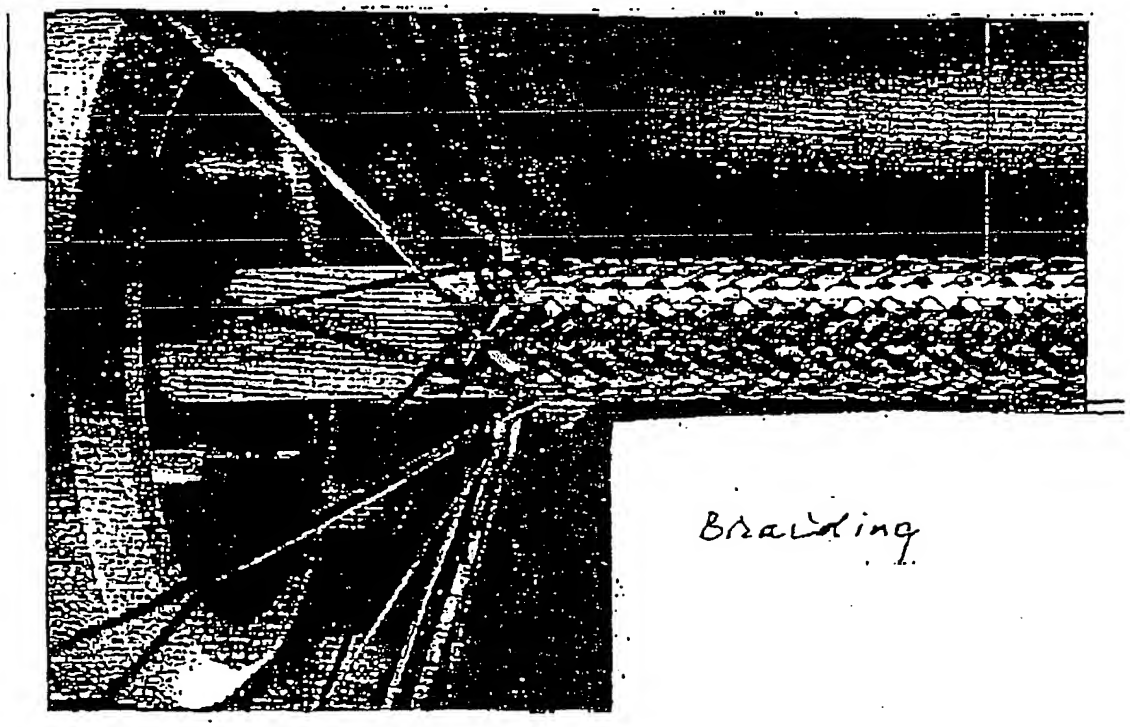

Fig 6

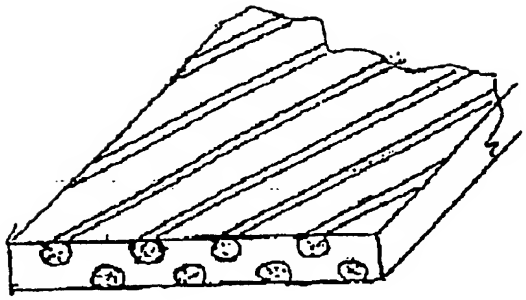

Fig 7

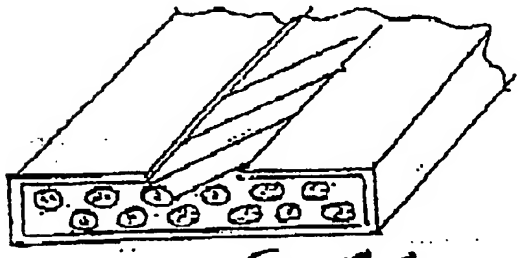

Fig 8

Fig 9

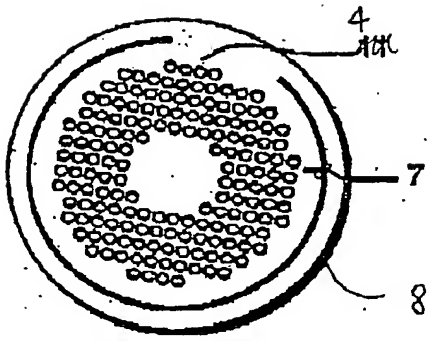

FIG. 10

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
26 October 2000 (26.10.2000)

PCT

(10) International Publication Number
WO 00/63456 A3

(51) International Patent Classification[7]: C23C 2/00, H01L 39/00, H01B 12/00

(21) International Application Number: PCT/US00/10464

(22) International Filing Date: 18 April 2000 (18.04.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

60/130,079	20 April 1999 (20.04.1999)	US
60/144,430	16 July 1999 (16.07.1999)	US
60/165,099	12 November 1999 (12.11.1999)	US
09/532,362	21 March 2000 (21.03.2000)	US

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(81) Designated States *(national)*: CN, JP.

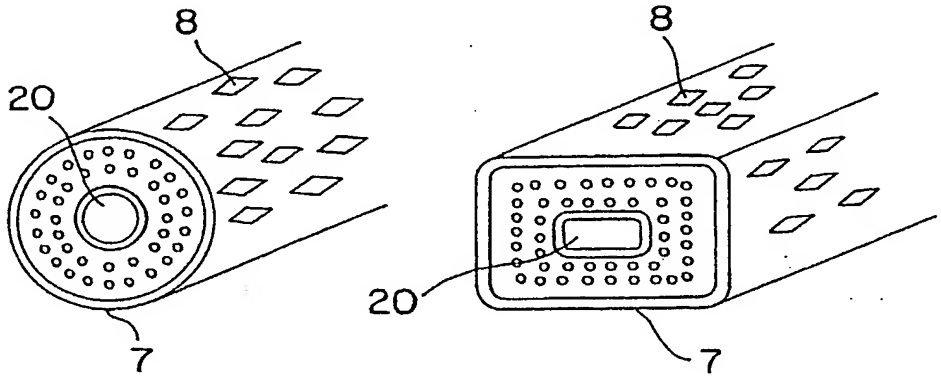
(84) Designated States *(regional)*: European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published:
— *with international search report*

(88) Date of publication of the international search report:
2 August 2001

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: CONSTRAINED FILAMENT NIOBIUM-BASED SUPERCONDUCTOR COMPOSITE AND PROCESS OF FABRICATION



(57) Abstract: A niobium-based superconductor is manufactured by establishing multiple niobium components in a billet of a ductile metal, working the composite billet through a series of reduction steps to form the niobium components into elongated elements, each niobium element having a thickness on the order of 1 to 25 microns, surrounding the billet prior to the last reduction step with a porous confining layer of an acid resistant metal, immersing the confined billet in an acid to remove the ductile metal from between the niobium elements while the niobium elements remain confined by said porous layer, exposing the confined mass of niobium elements to a material capable of reacting with Nb to form a superconductor.

WO 00/63456 A3

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C23C2/00 H01L39/00 H01B12/00

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IPC 7 C23C B32B H01L H01B

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	US 5 174 831 A (RUDZIAK MARK K ET AL) 29 December 1992 (1992-12-29) the whole document	1-11
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1 September 2000	20.10.00

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 00/10464

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